

PROCESS CHEMISTRY FOR THE PRE-TREATMENT OF HANFORD TANK WASTES

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PROCESS CHEMISTRY FOR THE PRETREATMENT OF HANFORD TANK WASTES

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ABSTRACT

Current guidelines for disposing radioactive wastes stored in underground tanks at the U.S. Department of Energy's Hanford Site call for the vitrification of high-level waste in borosilicate glass and disposal of the glass canisters in a deep geologic repository. Low-level waste is to be cast in grout and disposed of on site in shallow burial vaults. Because of the high cost of vitrification and geologic disposal, methods are currently being developed to minimize the volume of high-level waste requiring disposal.

Two approaches are being considered for pretreating radioactive tank sludges: 1) leaching of selected components from the sludge and 2) acid dissolution of the sludge followed by separation of key radionuclides. The leaching approach offers the advantage of simplicity, but the acid dissolution/radionuclide extraction approach has the potential to produce the least number of glass canisters.

Four critical components (Cr, P, S, and Al) were leached from an actual Hanford tank waste - Plutonium Finishing Plant sludge. The Al, P, and S were removed from the sludge by digestion of the sludge with 0.1 M NaOH at 100°C. The Cr was leached by treating the sludge with alkaline KMnO₄ at 100°C. Removing these four components from the sludge will dramatically lower the number of glass canisters required to dispose of this waste.

The transuranic extraction (TRUEX) solvent extraction process has been demonstrated at a bench scale using an actual Hanford tank waste. The process, which involves extraction of the transuranic elements with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), separated 99.9% of the transuranic

^(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

elements from the bulk components of the waste. Several problems associated with the TRUEX processing of this waste have been addressed and solved.

INTRODUCTION

Methods are being developed to treat and dispose of large volumes of radioactive wastes stored in underground tanks at the U.S. Department of Energy's (DOE) Hanford Site. Under current guidelines, the high-level waste (HLW) will be vitrified into borosilicate glass and disposed of in a geologic repository, while the low-level waste (LLW) will be converted to grout and disposed of by shallow burial on the Hanford Site. Because of the high cost of vitrification and geologic disposal, pretreatment methods are being developed to minimize the volume of HLW requiring disposal.

In this paper, we discuss two general approaches that are being considered for pretreating Hanford tank sludges. In the first approach, critical components are leached from the sludges while leaving the transuranic (TRU) elements in the sludge. In the second approach, acid dissolution of the sludges is followed by separating the TRU elements from the bulk sludge components using the transuranic extraction (TRUEX) process (1,2,3).^(b)

The plant that is to be used to vitrify HLW at Hanford utilizes a liquid-fed ceramic melter. Certain elements in the vitrification feed cause problems in operating the melter. For example, Cr can form an undesirable crystalline phase which can cause problems in operating the vitrification plant. Thus, the limits for Cr in the vitrification feed are low.

For any given waste, a critical component is present that defines the minimum number of glass canisters required to dispose of that waste. In the case of Hanford Plutonium Finishing Plant (PFP) sludge,^(c) the critical component is Cr. The next critical

^(b) Depending on the composition of the waste and the specifications for the LLW form, additional radionuclides (e.g., ⁹⁰Sr) might also need to be removed.

^(c) The PFP sludge consists of the neutralized raffinate from a tributyl phosphate (TBP) extraction process for recovering Pu from scrap materials. This process was conducted in the Plutonium Finishing Plant at Hanford. Miscellaneous other

component is P; that is, if the Cr were removed from this sludge, P would become the limiting component. The third and fourth critical components are S and Al, respectively. Removing the critical component results in lowering the number of glass canisters required to dispose of the waste (Table 1). Methods to leach these four components from PFP sludge will be described in this paper.

An alternative approach to the pretreatment of Hanford tank sludges is to dissolve the sludge in acid and separate the relatively small amount of TRU elements present from the bulk sludge components.^(a) The TRUEX process is being developed for this purpose (1,2,3). This process is a solvent extraction process in which the TRUs are extracted from nitric acid solution using octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). In this paper, we will discuss the TRUEX processing of another unique Hanford waste - neutralized cladding removal waste (NCRW) sludge.^(d)

EXPERIMENTAL

Leaching of PFP Sludge

A 0.65 g sample of PFP sludge was mixed with 5 mL of 0.1 M NaOH and the slurry was heated at 100°C for 1 h. After cooling, the mixture was centrifuged and the supernatant liquid was decanted. This treatment with 0.1 M NaOH was repeated three more times.

The PFP sludge was then mixed with 10 mL 0.014 M KMnO₄ in 0.1 M NaOH at 100°C for 1 h. After cooling, the mixture was centrifuged and the leach solution was

wastes have also been added to the tank containing this sludge. The sludge consists primarily of Fe, Al, Cr, Mn, and Ca oxides/hydroxides contaminated with TRUs and various fission products.

^(d) NCRW sludge was formed by the neutralization of the solution formed by chemical decladding of Zircaloy-clad metallic uranium fuel by the Zirflex Process (4). The sludge consists primarily of Zr(OH)₄ and NaF. It also contains U, TRUs (Am + Pu ~ 1000 nCi/g sludge), and mixed fission products (¹³⁷Cs, ⁹⁰Sr, ¹²⁵Sb, etc.).

decanted. The leached sludge was dissolved for analysis by heating at 100°C with 13.5 mL 1.8 M HCl/1.1 M HF.

All of the solutions were analyzed for Al, Cr, Fe, and P by inductively coupled plasma atomic emission spectroscopy (ICP). Ion chromatographic analyses were done to determine the PO_4^{3-} and SO_4^{2-} content of each solution.

TRUEX Processing of NCRW Sludge

A 2.45 g portion of NCRW sludge was slurried with 19 mL of water. Nitric acid (3.8 mL of 15.7 M) was added dropwise with stirring. After the last addition of HNO_3 , the mixture was stirred for 2 h at room temperature. The dissolved NCRW sludge solution was clarified by filtration through a 0.2- μm membrane filter.

To prepare the feed for the solvent extraction process, 8.33 mL of water and 0.63 mL of 15.7 M HNO_3 were added to 15.0 mL of the dissolved NCRW sludge solution. After 0.35 mL of this solution was removed for various analyses, 0.24 mL of 1 M $\text{H}_2\text{C}_2\text{O}_4$ was added to complete preparation of the aqueous phase for the first extraction contact. This solution represented a blend of the feed solution and the three scrub streams shown in Figure 1.

The TRUEX solvent used consisted of 0.2 M CMPO plus 1.4 M tri-n-butyl phosphate (TBP) dissolved in a normal paraffin hydrocarbon (NPH). It was washed with aqueous carbonate solution prior to use.

Eight milliliters of the TRUEX solvent was mixed with 24 mL of the feed solution for 30 seconds. The mixture was centrifuged to ensure separation of the two phases. Portions of both the organic and aqueous phases were subjected to additional contacts as summarized in Table 2.

The concentrations of nonradioactive metal ions were determined by ICP analysis. Analyses for alpha-emitting radionuclides involved counting 0.1-mL dried mounts of diluted samples from the aqueous phase of each contact. Concentrations of the various components in the organic phases were calculated by mass balance. Total fluoride concentrations were determined potentiometrically using a fluoride-selective electrode,

and acid content was determined by potentiometric titration with standard NaOH. The acid concentrations reported in this paper represent the concentration of HNO₃ + HF. The endpoints of the titrations were taken to be at pH 7, and the acid concentrations were corrected for the contribution of hydrolyzable ions using the following equation: $[H^+] = [H^+]_{total} - 2[Zr] - 3([Al] + [Fe] + [Cr])$.

RESULTS AND DISCUSSION

Leaching of PFP Sludge

When a portion of PFP sludge was digested with 0.1 M NaOH at 100°C, virtually all of the PO₄³⁻ and SO₄²⁻, and most of the Al, was removed from the sludge (Table 3). A fraction (27.1%) of the Cr originally present in the sludge was also removed by this treatment. This portion of the Cr was present as CrO₄²⁻ (as determined spectrophotometrically), so it was readily soluble in 0.1 M NaOH. The remaining Cr in the sludge was in the +3 oxidation state; thus, to leach the remaining Cr from the sludge it was oxidized to CrO₄²⁻ with KMnO₄.

The oxidation of Cr(III) to Cr(VI) with MnO₄⁻ proceeds in basic solution according to the following equation:



For every mole of Cr leached from the sludge, one mole of Mn is added to the sludge in the form of MnO₂. The addition of Mn to the sludge is acceptable because the limit for Mn in the vitrification feed is ten times the limit for Cr. However, by using MnO₄⁻ to leach Cr, Mn becomes the critical component in the waste. It is estimated that if Al, P, and S were removed by digestion in dilute NaOH, and Cr was removed by leaching with MnO₄⁻, 420 canisters of glass would be required to dispose of the PFP sludge. This number could be lowered to approximately 300 canisters (Table 1) if a different oxidant were used. We are currently evaluating alternative oxidants for this purpose.

If the PFP sludge is pretreated using the TRUEX process, it is expected that the number of glass canisters required to dispose of the TRU fraction of the waste will be defined by the amount of the sludge that does not dissolve in HNO_3 . Dissolution tests conducted in our laboratory suggest that approximately 100 canisters would be required if the PFP sludge were dissolved and processed using TRUEX. Thus, the TRUEX approach would result in a smaller number of glass canisters being produced from PFP sludge than would the leaching approach. However, the TRUEX process would be much more difficult to implement than the simple leaching methods described here.

TRUEX Processing of NCRW Sludge

The flowsheet describing the experiment performed to test an early concept for the TRUEX processing of NCRW sludge is shown in Figure 1. The experiment done to test this flowsheet consisted of the following steps: 1) sludge dissolution and solution clarification by filtration, 2) adjustment of the solution so that it represented a blend of the feed and the three scrub streams shown in Figure 1, 3) extraction, 4) scrubbing (with three different streams), and 5) stripping. The functions of the three scrub streams were to 1) remove extracted Zr and F with aqueous $\text{H}_2\text{C}_2\text{O}_4$, 2) remove extracted $\text{H}_2\text{C}_2\text{O}_4$ with HNO_3 , and 3) remove extracted HNO_3 with water.

Unwashed NCRW sludge dissolved readily in dilute HNO_3 . In the treatment with HNO_3 , 97.8% of the Zr and virtually 100% of the Na dissolved. Significant amounts of Al (25%) and P (43%) did not dissolve in HNO_3 . The adjusted feed solution consisted of 0.10 M Zr, 1.14 M Na, 0.049 M K, 0.045 M Al, 0.035 M Si, 0.004 M U, 0.37 M F, and 1.68 M H^+ . The feed solution also contained 62.0 nCi/mL Pu and 9.5 nCi/mL Am.

The results of the extraction contacts are shown in Figure 2. The TRUs were effectively extracted from the dissolved NCRW solution. The distribution coefficients for the TRUs in the first and second extractions were 69 and 34, respectively; and that for the third extraction contact was approximately 6. The raffinate from the third extraction contained only 0.1% of the TRU activity originally present in the feed. A significant

amount of Zr was extracted, but Na and Al were not. As expected from published data (1), a large fraction of the HNO_3 was extracted.

The small portion of Zr that was extracted was removed from the solvent during the first three scrub contacts (Figure 3). Zirconium could not be detected in solutions from subsequent contacts. Thus, $\text{H}_2\text{C}_2\text{O}_4$ is very effective at removing Zr from the extract. Of the fluoride that was extracted, 99.3% was scrubbed out after the sixth scrub contact; the data in Figure 3 suggest that the residual F^- may be difficult to remove from the extract. The results from scrubs five and six indicate that water can lower the acid content of the extract. Throughout the six scrub contacts, the TRUs remained in the organic phase.

The TRUs were efficiently stripped from the scrubbed extract (Figure 4) with 1-Hydroxyethane-1,1-diphosphonic acid (HEDPA). Over 99% of the TRUs were stripped in the first strip contact. The amount of TRUs present after the third strip was below detection limits.

These results serve as proof-of-principle that the TRUEX process can be used to separate TRUs from the bulk components (Zr and Na) of NCRW sludge. The extraction of the TRUs was very good; only ~ 0.1 nCi/mL of alpha activity remained in the aqueous phase after the third extraction. Good separation of the alpha-emitting radionuclides from most nonradioactive materials was achieved. For example, the feed solution contained ~ 7800 nCi TRU per g of Zr, but the aqueous phase from the third extraction contained only 11 nCi per g Zr. Likewise, the feed solution contained ~ 4400 nCi TRU per g of Na, whereas the aqueous phase from the third extraction contained only 5 nCi TRU per g Na. Elements that were not well separated from the alpha emitters were U and the lanthanides (e.g. La, Ce, and Eu).

However, further study identified some problems with the TRUEX processing of NCRW sludge, such as

- corrosion of stainless steel piping and equipment
- precipitation from dissolved NCRW sludge solutions
- interfacial crud formation in the extraction step
- excessive quantity of HEDPA stripping agent.

Each of these problems has been addressed and solved, as is discussed below.

Originally, it was planned to implement the TRUEX process in an existing facility (B-Plant) at Hanford. Corrosion tests with simulated dissolve NCRW solutions indicated that the imbedded piping in this plant might be susceptible to corrosion during the TRUEX processing of NCRW sludge. Recently, it has been determined that B-Plant will not be used to process Hanford tank wastes; rather, a new pretreatment facility will be built. Thus, corrosion of piping in B-Plant was rendered a non-problem. Corrosion should not be a problem in the new facility because appropriate alloys will be chosen for construction.

During the course of many experiments with actual NCRW samples, it was discovered that solids formed in dissolved sludge solutions at sporadic intervals, that ranged from weeks to days. The formation of precipitates in the dissolved sludge solution was deemed to be a problem because this would require additional equipment clean-out capability.

In these early experiments, the NCRW sludge samples were dissolved in HNO_3 directly. It was discovered that washing the sludge with water prior to acid dissolution resulted in dissolved sludge solutions that were stable for weeks to months (Table 4). Washing the sludge lowers the Na and F content. In order to achieve adequate sludge dissolution, F must be added during the dissolution step so that the $\text{F}/(\text{Zr} + \text{Al})$ ratio is approximately 2. This can be done by adding HF along with HNO_3 during dissolution. Solutions prepared by dissolving washed NCRW sludge in this manner are sufficiently stable that equipment clean-out capability is not expected to be needed.

The third problem associated with the TRUEX processing of NCRW sludge was interfacial crud forming during the extraction step. Although no crud was observed in the above described experiment, interfacial crud was observed in some TRUEX experiments with dissolved NCRW solutions. In some cases, the amount of crud was so severe that the entire organic phase was filled with solids.

Further studies revealed that interfacial crud can be controlled by adjusting the $F/(Zr + Al)$ ratio in the solvent extraction feed. Figure 5 summarizes the interfacial crud observations from a number of experiments with dissolved NCRW solutions. Solutions were prepared from both washed and unwashed sludges. In all cases, the feed solutions were aged a minimum of 1 h prior to contacting with the TRUEX solvent; the organic-to-aqueous phase ratio was 0.33 in each contact. Although the process conditions have not yet been fully optimized, the data in Figure 5 suggest that the concentration of Zr in the extraction stages should be maintained below 0.15 M and the $F/(Zr + Al)$ ratio greater than 4. The $F/(Zr + Al)$ ratio can be adjusted by adding HF to the dissolved sludge solution. We have observed that increasing the $F/(Zr + Al)$ ratio does not have an immediate effect in eliminating interfacial crud, so a lag time of 1 h should be allowed between adding HF and beginning the extraction step.

The composition of the interfacial crud has not been determined, but it is presumed to contain a Zr species. The crud forms when the concentration of this species in the organic phase exceeds its solubility. Complexation of Zr by F^- lowers the distribution coefficient for Zr; thus, raising the $F/(Zr + Al)$ decreases the extraction of Zr and the crud does not form.

The fourth problem with the TRUEX processing of NCRW sludge concerns using 0.2 M HEDPA as the stripping solution. Although this solution performs very well in stripping the TRUs from the extract (Figure 4), the phosphorus content of this solution will cause problems in subsequent processing, namely, in the vitrifying the TRU fraction of the waste. Several alternative stripping solutions have been identified [e.g. sodium citrate, 0.002 M HEDPA + 0.25 M Na_2CO_3 (5), ferrous sulfamate, etc.]. A final decision has not been made on which strip solution will be used.

CONCLUSION

Two different approaches are being investigated for reducing the quantity of HLW needing disposal at the Hanford Site. Selective leaching of glass-limiting components is a method applicable in selected cases and is easy to implement. Simple methods have been demonstrated for leaching Cr, P, S, and Al from PFP sludge. The second approach--sludge dissolution and extraction of TRUs--is generally applicable and will likely result in a greater reduction in quantity of HLW needing disposal. Batch testing of the TRUEX process on actual NCRW sludge indicates that this process will effectively separate the TRU component of this waste from the bulk sludge materials.

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FIGURE CAPTIONS

- Figure 1. Flowsheet for the pretreatment of NCRW sludge by the TRUEX process.
- Figure 2. Results of the extraction contacts in the experiment testing the flowsheet in Figure 1.
- Figure 3. Results of the scrub contacts in the experiment testing the flowsheet in Figure 1.
- Figure 4. Results of the stripping contacts in the experiment testing the flowsheet in Figure 1.
- Figure 5. Interfacial crud formation in TRUEX contacts with dissolved NCRW sludge. The $F/(Zr + Al)$ ratio was adjusted as appropriate by addition of HF to the aqueous solutions. A minimum of one hour was allowed before contacting with the TRUEX process solvent.

Table 1. Effect of the Removal of Critical Components from PFP Sludge on the Number of Glass Canisters Required to Dispose of this Waste.

Option	No. of Canisters Needed	Limiting Component
Sludge Wash (SW) Only	2480	Cr
SW+Cr removal	1230	P
SW+Cr+P removal	750	S
SW+Cr+P+S removal	680	Al
SW+Cr+P+S+Al removal	300	Other

Table 2. Summary of TRUEX Solvent Extraction Contacts Performed To Test the Flowsheet Depicted in Figure 1.

Contact	Step	Aqueous Phase	Organic Phase	O/A ^(a)	Organic Vol., mL
A	Extn 1	Feed ^(b)	TRUEX Solvent	0.33	8.00
B	Extn 2	From A	TRUEX Solvent	0.33	1.00
C	Extn 3	From B	TRUEX Solvent	0.33	0.67
D	Scrub 1	1.5 <u>M</u> HNO ₃ + 0.05 <u>M</u> H ₂ C ₂ O ₄ ^(c)	From A	1.00	7.00
E	Scrub 2	1.5 <u>M</u> HNO ₃ + 0.05 <u>M</u> H ₂ C ₂ O ₄	From D	1.00	6.00
F	Scrub 3	2.3 <u>M</u> HNO ₃ ^(d)	From E	1.50	5.00
G	Scrub 4	2.3 <u>M</u> HNO ₃	From F	1.50	4.00
H	Scrub 5	Water	From G	3.00	3.50
I	Scrub 6	Water	From H	3.00	3.00
J	Strip 1	0.21 <u>M</u> HEDPA ^(e)	From I	3.00	2.50
K	Strip 2	0.21 <u>M</u> HEDPA ^(e)	From J	3.00	2.00
L	Strip 3	0.21 <u>M</u> HEDPA ^(e)	From K	3.00	1.50
M	Wash	0.25 <u>M</u> Na ₂ CO ₃	From L	1.00	1.00

(a) O/A = Volume of the organic phase divided by the volume of the aqueous phase.

(b) The feed solution was a diluted dissolved NCRW sludge solution (see text).

(c) Composition represents a blend of the three scrub streams shown in Figure 1.

(d) Composition represents a blend of the second and third scrub streams shown in Figure 1.

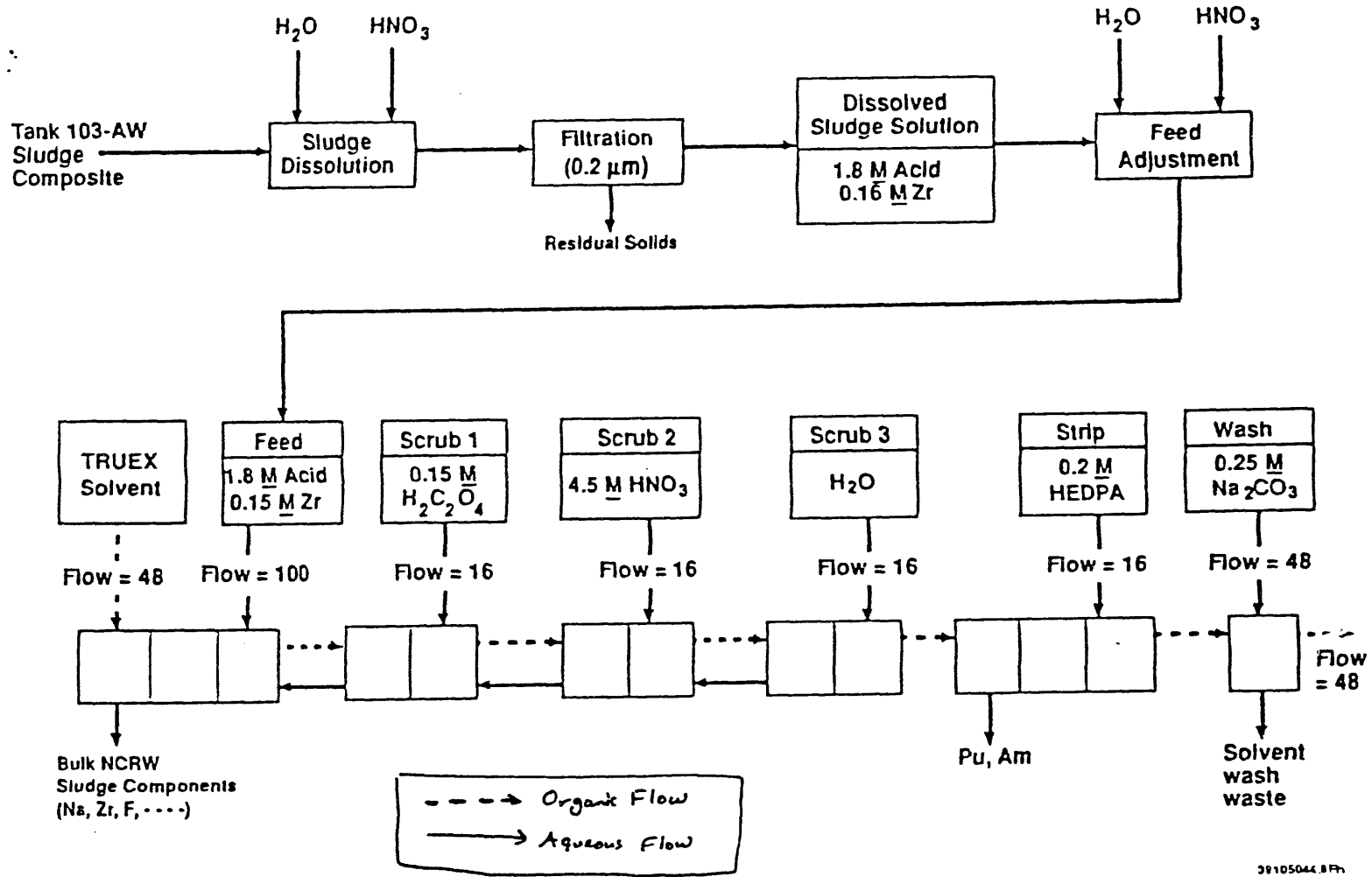
(e) HEDPA = 1-Hydroxyethane-1,1-diphosphonic acid.

Table 3. Results from the Leaching of PFP Sludge.

	Al	Cr	P	S	Fe
% in NaOH wash	69.1	27.1	100	100	0.2
% in KMnO ₄ leach	29.8	69.3	0	0	0
% in leached sludge	1.1	3.6	0	0	99.8

Table 4. Stability of Dissolved Sludge Solutions Toward Precipitation.

Zr, <u>M</u>	Al, <u>M</u>	Na, <u>M</u>	H ⁺ , <u>M</u>	F/(Zr + Al)	Days Stable
Unwashed Sludge:					
0.24	0.053	1.78	0.6	2.9	>1, <2
0.10	0.023	0.76	1.4	2.9	>1, <2
0.13	0.015	1.75	1.2	2.0	>20
Washed Sludge:					
0.18	0.006	0.20	1.7	1.8	>170
0.16	0.002	0.07	1.7	2.3	>5, <34
0.13	0.011	0.06	1.8	2.5	>225
0.12	0.001	0.05	1.5	1.3	>150



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Design Basis Experiment

Fig. 1

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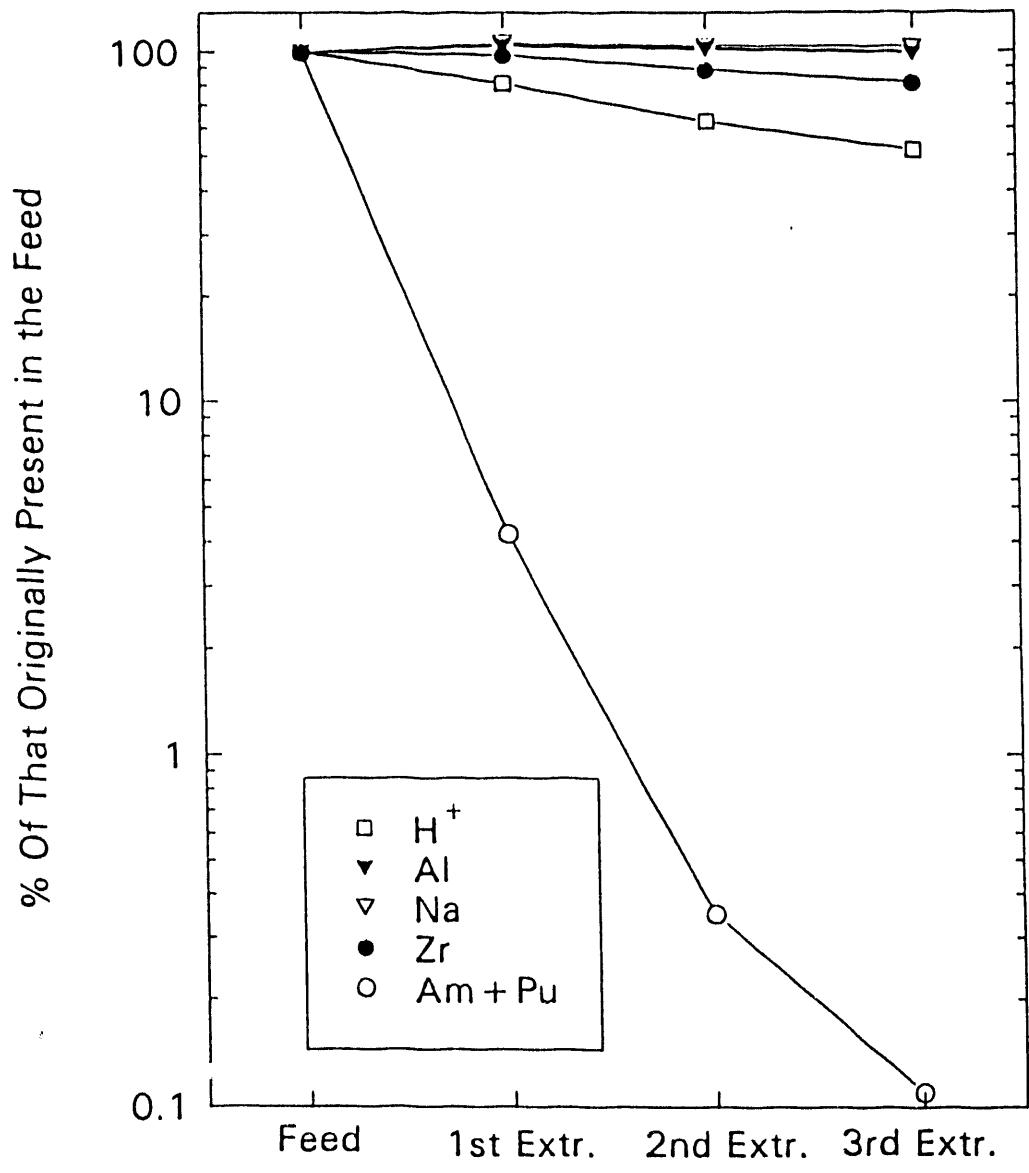
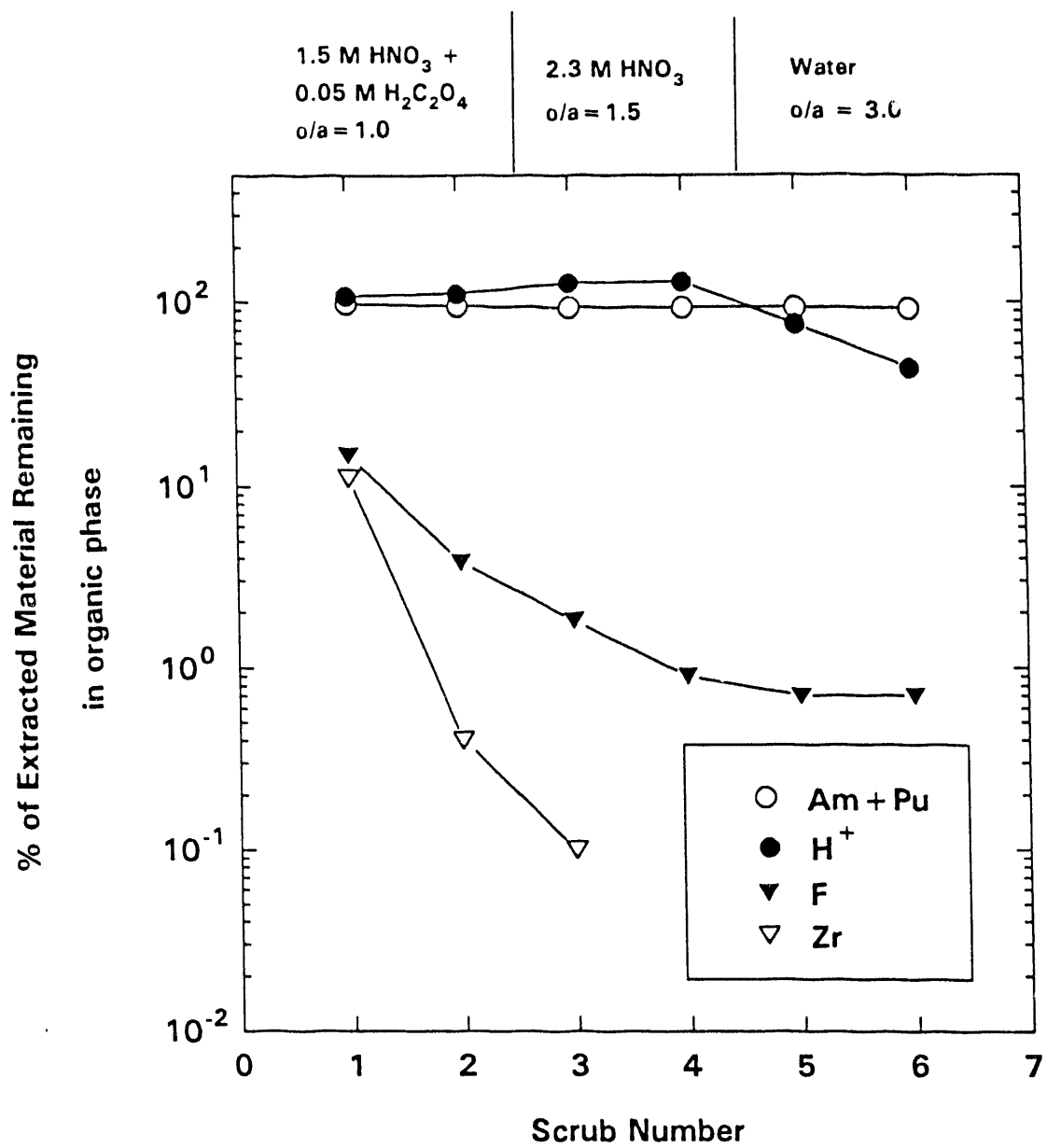


Fig 2



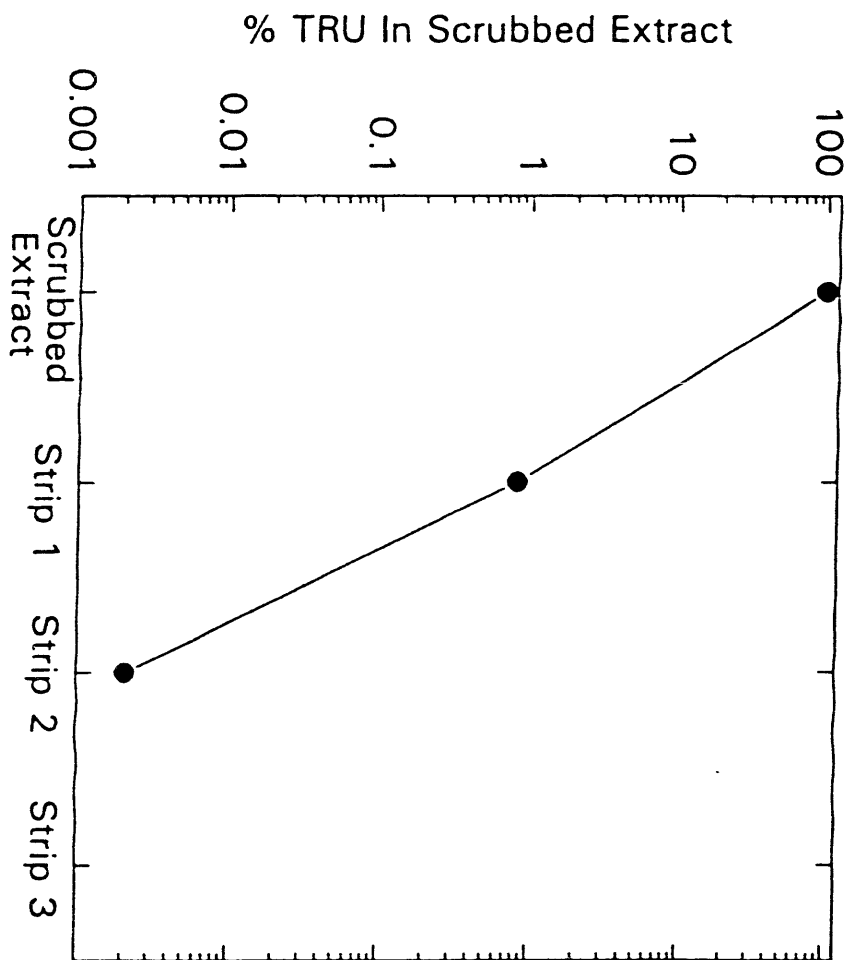


Fig 4

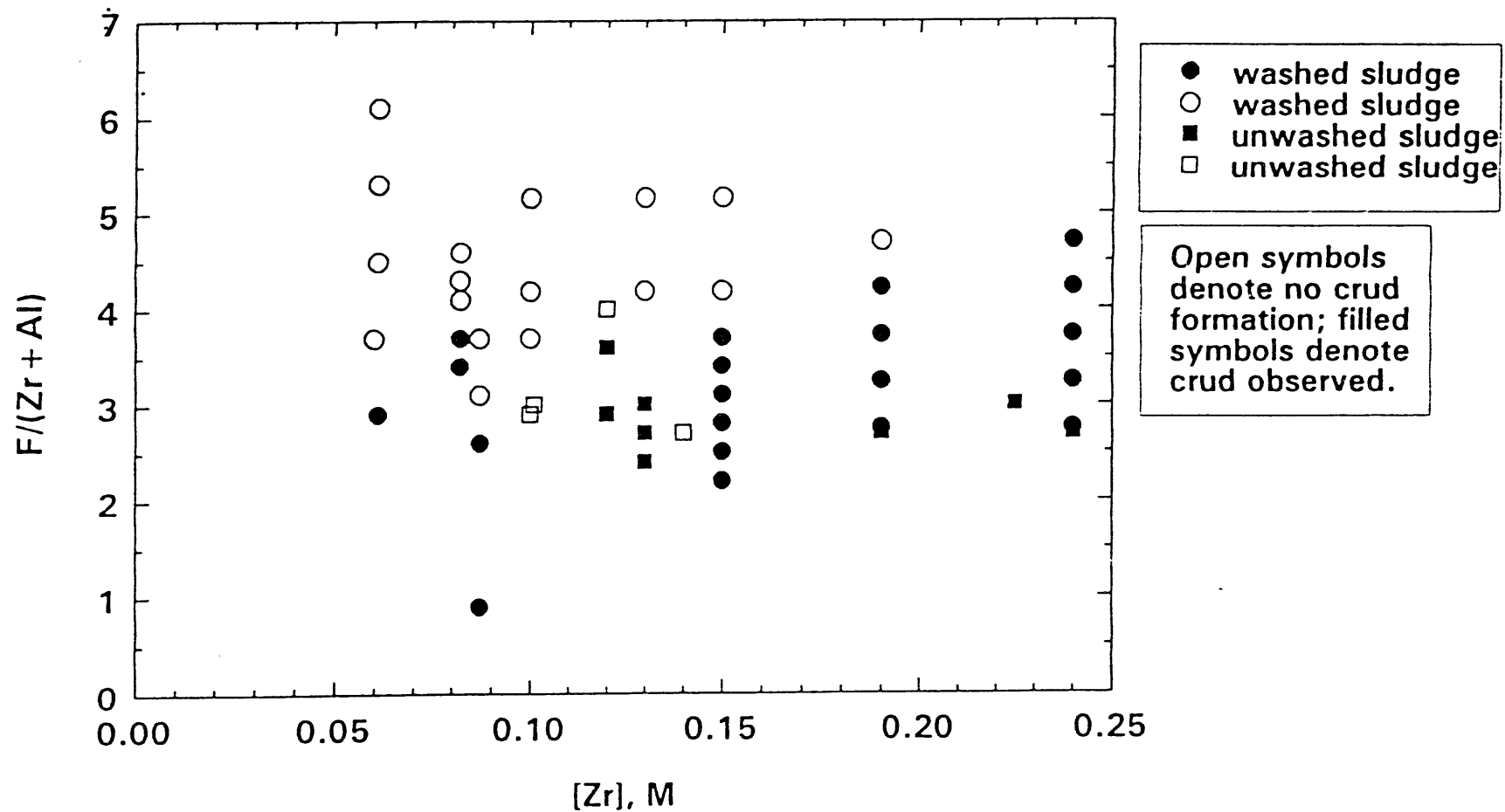


Fig 5

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